

524,982

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 March 2004 (04.03.2004)

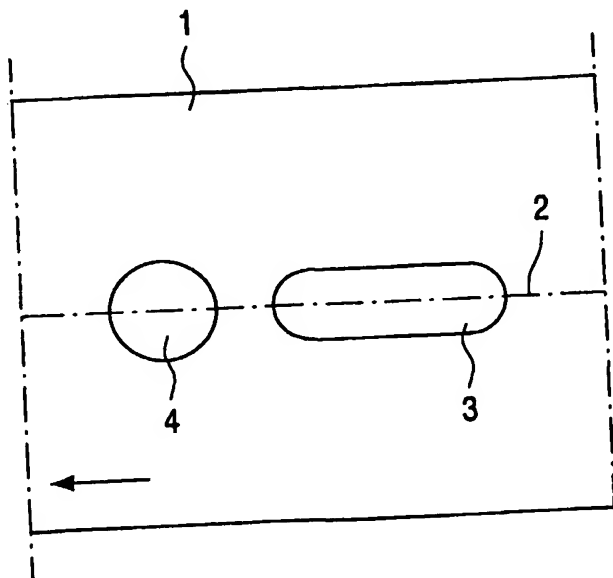
PCT

(10) International Publication Number
WO 2004/018144 A1

- (51) International Patent Classification⁷: **B23K 26/14**, (74) Agent: **DEGUELLE, Wilhelmus, H., G.**; Philips Intellectual Property & Standards, Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).
- (21) International Application Number: **PCT/IB2003/003271** (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 18 July 2003 (18.07.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 21 August 2002 (21.08.2002) EP (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): **KONINKLIJKE PHILIPS ELECTRONICS N.V.** [NL/NL]; Groenewoudseweg 1, NL-5621 BA Eindhoven (NL).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **BRZESOWSKY, Rudolf, H.** [NL/NL]; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). **BALKENENDE, Abraham, R.** [NL/NL]; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). **VAN AGTHOVEN, Raymond, G., A.** [NL/NL]; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). **TIMMERMANS, Petrus, H., M.** [NL/NL]; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). **WILLARD, Nicolaas, P.** [NL/NL]; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).
- Declaration under Rule 4.17:**
— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN,

[Continued on next page]

(54) Title: METHOD OF BREAKING A BRITTLE SUBSTRATE



(57) Abstract: The invention relates to a method of breaking a substrate of a brittle material, the method comprising the steps of providing a substrate (1) of a brittle material, heating the substrate with a laser beam (3) to create a heated spot on the substrate, moving the laser beam and the substrate with respect to each other to create a line of heated spots on the substrate (2), cooling the heated spots on the substrate by locally applying a cooling medium (4) behind the heated spots such that a micro-crack is propagated in the line of heated spots, and breaking the substrate along the line of the propagated micro-cracks by applying a mechanical force on the substrate wherein the cooling medium comprises an aqueous surfactant solution. The surfactants will connect to the broken siloxane bonds inside the surface cracks. Then recombination and healing of the broken siloxane bonds will not occur and the required breaking load will remain constant over time.

WO 2004/018144 A1



TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Method of breaking a brittle substrate

The invention relates to a method of breaking a substrate of brittle material, the method comprising the steps of providing a substrate of a brittle material, heating the substrate with a laser beam to create a heated spot on the substrate, moving the laser beam and the substrate with respect to each other to create a line of heated spots on the substrate, cooling the heated spots on the substrate by locally applying a cooling medium such that a micro-crack in the line of heated spots is propagated, and breaking the substrate along the line of micro-cracks by applying a force on the substrate.

Many products made from a brittle non-metallic material, e.g. glass and semiconductor wafer materials, are formed by separating a piece, sheet, wafer, or panel into a number of smaller pieces of the desired size or sizes.

US-6,252,197 discloses a method for physically separating brittle substrates by forming a micro-crack in the substrate and controllingly propagating the micro-crack. An initial mechanical or laser scribing device forms a micro-crack in the substrate. A laser beam is applied onto the substrate on a separation line. A coolant stream comprising a mixture of pressurized gas and water intersects with the trailing edge of the laser beam. The temperature differential between the heat affected zone of the substrate and the coolant stream propagates the micro-crack. By applying a mechanical load the substrate is subsequently broken into smaller pieces along the separation line, which may be further processed e.g. to produce display devices.

It is a problem connected to this method that the mechanical load necessary to further open the induced surface cracks increases with time, i.e. the mechanical load is higher the longer the time elapsed between the moment of inducing micro-cracks and the final breaking of the substrate into smaller pieces. This is undesired since in a factory it is often not possible to immediately break the substrates after they have been treated with the laser beam. In that case the subsequent breaking of the substrate results in damage of edges and a lower production yield.

It is an object of the invention to provide a breaking process in which the breaking load remains constant over time after the initiation of micro-cracks. To this end the method according to the invention is characterized in that the cooling medium comprises an aqueous surfactant solution. The inventors have realized that the increase of the breaking load
5 in the conventional process is due to locking or even healing of the micro-cracks. However, if the cooling medium comprises an aqueous surfactant solution the surfactants will connect to the broken siloxane bonds inside the micro-cracks. Recombination and healing of the broken siloxane bonds will not occur and the required breaking load will remain constant over time. Furthermore, the surfactants will change (i.e. lower) the surface energy of the cracks.
10 Consequently, the cracks will be kept open and the load needed to open the cracks will be lowered.

The dependent claims describe advantageous embodiments of the invention.

These and other objects of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter.

15 In the drawings:

Fig. 1 is a schematic view from above of an apparatus employing the method according to the invention, and

20 Fig. 2 shows results of load measurements for various cooling media and various elapsed times.

The figures are not drawn to scale. In the figures, like reference numerals generally refer to like parts.

Fig. 1 is a schematic view from above of an apparatus employing the method
25 according to the invention. A spot 3 of a laser beam is focussed on substrate 1 of a brittle material, e.g. glass, crystalline silica, ceramics or compositions thereof. The energy contained in the laser spot 3 causes local heating of the substrate. A cooling medium from a nozzle 4 in the vicinity of the laser spot 3 (in most cases positioned behind the laser spot) cools the heated spot. This rapid temperature differential causes a thermal shock and causes a pre-
30 existing micro-crack to propagate.

The substrate is moved with respect to the laser spot in a direction indicated by the arrow. Likewise, the laser beam may be moved with respect to the substrate in a direction opposite to the arrow. As a result of the relative movement the micro-crack is propagated along a separation line 2.

Next, the substrate 1 can be broken along the separation line 2 in a conventional way by exerting a mechanical load force to the substrate.

It has been observed that the mechanical load required to break the substrate depends on the amount of time elapsed between the formation of the micro-cracks and the moment of applying the mechanical load. Fig. 2 shows results of load measurements for various cooling media and various elapsed times. The data are provided with bars indicating the statistical spread on the measurements. Displayed is the required mechanical load (in Newton) for breaking the substrate in case of:

- a spray mixture of air and ethanol as cooling medium, 30;
- cooling by a spray mixture of air and water, and immediately followed by breaking, 40;
- cooling by a spray mixture of air and water, and breaking after 12 hours, 50;
- cooling by a spray mixture of air and an aqueous solution comprising 0.1% by weight of the surfactant cetyl trimethyl ammonium bromide (CTAB) and immediate breaking, 60;
- cooling by a spray mixture of air and an solution of water comprising 0.1% by weight of the surfactant cetyl trimethyl ammonium bromide (CTAB) and breaking after 15 hours, 70.

For reasons of comparison the mechanical load for the conventional mechanical scribe process is also indicated, 20.

From the data shown in Fig. 2 it can be concluded that the mechanical load is reduced by almost a factor of 2 if CTAB is used and that the reduction remains if breaking occurs after 15 hours. Good process yield was obtained when the glass plates were further processed and LCD panels were made from them.

CTAB is a compound belonging to the class of cationic surfactants, i.e. a surface active agent, a substance such as a detergent that reduces the surface tension of a liquid. Good results were also obtained with compounds belonging to the classes of non-ionic and anionic surfactants, such as octadecyl deca(ethyleneoxide) hydroxide or dodecylbenzene sulfonic acid sodium salt, respectively. All compounds have in common their capability of binding to the broken siloxane bonds ('dangling bonds') inside the micro-cracks.

Good results were obtained when the compounds were present in the aqueous solution in the range of 0.01 to 1 % by weight.

In summary, the invention relates to a method of breaking a substrate of brittle material, the method comprising the steps of providing a substrate 1 of a brittle material, heating the substrate with a laser beam 3 and creating a heated spot on the substrate, moving the laser beam and the substrate with respect to each other thus creating a line of heated spots

on the substrate 2, cooling the heated spots on the substrate by locally applying a cooling medium 4 behind the heated spots such that a micro-crack is propagated in the line of heated spots, breaking the substrate along the line of the propagated micro-cracks by applying a mechanical force on the substrate wherein, the cooling medium comprises an aqueous surfactant solution.

It should be noted that the above-mentioned embodiments illustrate rather than limit the invention, and that those skilled in the art will be able to design many alternative embodiments without departing from the scope of the appended claims. In the claims, any reference signs placed between parentheses shall not be construed as limiting the claim. The word "comprising" does not exclude the presence of other elements or steps than those listed in a claim. The word "a" or "an" preceding an element does not exclude the presence of a plurality of such elements.

CLAIMS:

1. A method of breaking a substrate of brittle material, the method comprising the steps of:

- providing a substrate of a brittle material,
- heating the substrate with a laser beam to create a heated spot on the substrate,
- 5 – moving the laser beam and the substrate with respect to each other to create a line of heated spots on the substrate,
- cooling the heated spots on the substrate by locally applying a cooling medium such that a micro-crack in the line of heated spots is propagated, and
- breaking the substrate along the line of the propagated micro-crack by applying a force on
- 10 the substrate

wherein the cooling medium comprises an aqueous surfactant solution.

2. A method of breaking a substrate of brittle material according to claim 1, wherein the cooling medium further comprises air mixed with the aqueous surfactant

15 solution.

3. A method of breaking a substrate of brittle material according to claim 1, wherein the concentration of the surfactant is in the range of 0.01 to 1 % of weight.

20 4. A method of breaking a substrate of brittle material according to claim 1, wherein the aqueous surfactant solution comprises a cationic surfactant.

5. A method of breaking a substrate of brittle material according to claim 3, wherein the cationic surfactant comprises cetyl trimethyl ammonium bromide (CTAB).

25 6. A method of breaking a substrate of brittle material according to claim 1, wherein the aqueous surfactant solution comprises a nonionic surfactant.

7. A method of breaking a substrate of brittle material according to claim 5, wherein the nonionic surfactant comprises octadecyl deca(ethylenoxide) hydroxide.
8. A method of breaking a substrate of brittle material according to claim 1, wherein the aqueous surfactant solution comprises an anionic surfactant.
9. A method of breaking a substrate of brittle material according to claim 7, wherein the anionic surfactant comprises dodecylbenzene sulfonic acid sodium salt.
10. A method of breaking a substrate of brittle material according to claim 1, wherein the brittle material comprises glass, crystalline silica, ceramics or compositions thereof.

1/1

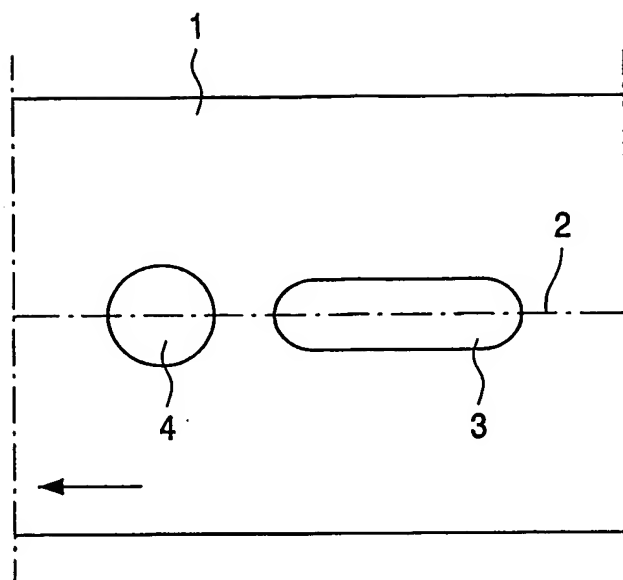


Fig.1

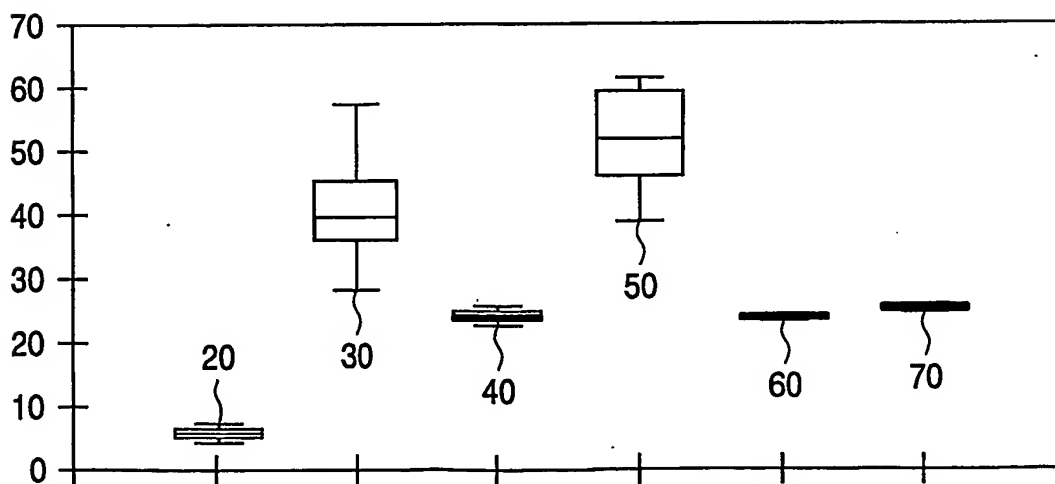


Fig.2

INTERNATIONAL SEARCH REPORT

PCT/IB 03/03271

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B23K26/14 C03B33/09 C03B33/095

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B23K C03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 2003/052098 A1 (CHOO DAE-HO ET AL) 20 March 2003 (2003-03-20) paragraph '0051! - paragraph '0053! paragraph '0056! paragraph '0068! paragraph '0072! - paragraph '0077!; claims 1,9,12; figures 4,5	1,10
A	US 6 252 197 B1 (KAR ARAVINDA ET AL) 26 June 2001 (2001-06-26) cited in the application the whole document	1,10
A	US 6 350 123 B1 (KIMMEL ANDREW I ET AL) 26 February 2002 (2002-02-26) the whole document	1,2,10

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

10 November 2003

Date of mailing of the international search report

25/11/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Aran, D

PC 03/03271

PC 03/03271

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 2003052098	A1	20-03-2003	KR	2002089711 A		30-11-2002
			JP	2002346995 A		04-12-2002
US 6252197	B1	26-06-2001	US	6259058 B1		10-07-2001
			US	6211488 B1		03-04-2001
			US	6420678 B1		16-07-2002
US 6350123	B1	26-02-2002	US	5741247 A		21-04-1998
			US	5785521 A		28-07-1998
			US	6567582 B1		20-05-2003
			US	6561803 B1		13-05-2003
			US	6254597 B1		03-07-2001
			US	6231567 B1		15-05-2001
			AU	7011796 A		19-03-1997
			EP	0847319 A2		17-06-1998
			JP	11511386 T		05-10-1999
			WO	9707928 A2		06-03-1997
			US	6610053 B1		26-08-2003